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CHEMISORPTION AND REACTIONS OF MOLECULES ON
SEMICONDUCTOR SURFACES(U) IBM THOMAS J WATSON RESEARCH
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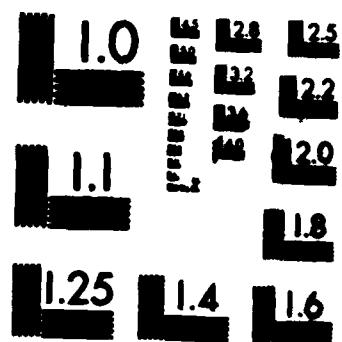
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We have performed experimental measurements of adsorbed atoms and molecules on metal and semiconductor surfaces over a wide range of temperatures (20K - 1000K) to identify the nature of bonding, the structure, reaction intermediates and reaction products. This has included simple hydrocarbon and organic molecules on Ni, Pd, Pt and Ag single-crystal surfaces. The techniques of UV photoemission, low energy electron diffraction and high resolution electron energy loss spectroscopy were used and further developed to extract new information. The electronically excited states of adsorbates relevant to Surface Enhanced Raman and Surface Chemistry were also investigated. Later work on Si(111) surfaces included studies of oxidation, water adsorption and metallization.

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1. *The valence orbital electronic excitations of CO chemisorbed on Ni(111) have been studied by Surface Reflectance Spectroscopy and show that fundamental electronic excitations were not strongly altered by chemisorption. Charge transfer excitations were also observed and identified (See Ref. 1).*
2. *Selection rule effects in valence orbital electron loss studies have been shown to suppress certain low-lying valence transitions for chemisorbed CO and unsaturated hydrocarbons on surfaces (see Ref. 2).*
3. *The dehydrogenation of cyclohexane to benzene on Pd and Pt(111) surfaces have been observed at room temperature by photoemission spectroscopy (see Ref. 3).*
4. *A pulsed gas dosing system has been developed which provides local pressures at the sample of 10² higher than the system and can be switched (on/off) in 2-3 msec. Used in conjunction with photoemission, the dose enabled the measurement of desorption kinetics of CO on Ni(111) up to temperatures of 230°C. Pre-exponential factors and desorption energies were determined and found to show significant variations with coverage (Ref. 4).*
5. *Pure $h\nu = 40.8$ eV radiation has been achieved by significantly increasing the He II light of our d.c. He resonance lamp and inserting a carbon filter. The filtered lamp provided for photoemission studies of entire valence band of chemisorbed molecules (Refs. 5, 6, 7, 8).*
6. *Low-lying C 2s-derived orbital shifts have been observed for chemisorbed unsaturated hydrocarbons and attributed to initial state potential effects (Ref. 5).*
7. *Photoemission and thermal desorption study of acetylene and ethylene exposed to Pt(111) at room temperature has shown the formation of new chemical species. A methodology of analyzing the*

valence levels was developed and suggests C-CH₂ and CH-CH₂ species form from acetylene and ethylene, respectively (Ref. 6).

8. *The conversion of C₂H₄ to C₂H₂ on Ni(111)* has been studied by photoemission and thermal desorption spectroscopy. Desorption of approximately half the initially chemisorbed ethylene occurs during the conversion. Models for the decomposition reactions proposed (Ref. 9).

9. *Molecular geometries of acetylene and ethylene chemisorbed on Ni(100), Ni(110), Ni(111), Pd(111) and Pt(111)* have been determined from the entire valence band ionization spectra. A methodology was developed to obtain geometric information from ionization spectra of adsorbed species via comparison to gas phase spectra and the calculated relative changes in the orbital energies upon geometric distortion (Ref. 7).

10. *An angle-resolved photoemission study of hydrogen chemisorbed on Ni(111)* has shown no split-off hydrogen-derived state. Direct transitions from sp-type bands are enhanced whereas d-like interband transitions remain unchanged (Ref. 10).

11. *The reaction of acetylene with Ni(100) and Ni(110) at room temperature* has been studied by photoemission and thermal desorption spectroscopy. A methodology for predicting ionization levels of new chemical species developed. CH and CCH species isolated and identified (Ref. 8).

12. *High-resolution electron energy loss studies of adsorbed species* have been done in collaboration with H. Ibach:

- a. *Observation of soft CH modes* and their relation to dehydrogenation reactions of ethylene on Ni(111) and cyclohexane on Pt(111) Ref. 11).
- b. *Identification of CH species* on Ni(111) (Ref. 12).
- c. *Isolation and identification of methoxy species* on Ni(111) (Ref. 13).
- d. *Chemical nature and bonding symmetry of benzene on Ni(111) and Pt(111)* determined (Ref. 14).



- e. *Chemical nature and bonding symmetry of chemisorbed acetylene on Ni(111) determined (Ref. 15).*
- 13. *Molecular orbital calculations have been used to investigate the force constants and dynamic dipole moments of acetylene bonded to Be atom clusters. The nature of dynamic surface charge coupling to C-C bond vibrations was investigated and related to surface studies (Ref. 16).*
- 14. *Photoemission bonding energy shifts in the core levels of surface atoms relative to bulk atoms are observed for Ir(111), Ir(100)-(5×1) and the metastable Ir(100)-(1×1) surfaces. These shifts provide information on the surface atom coordination number while surface atom core level emission give direct information on the number of surface atoms. The reconstructed Ir(100)-(5×1) surface is described by a compressed hexagonal layer (Ref. 17).*
- 15. *Combined LEED, UV photoemission, and Auger studies of the adsorption and reaction of silane and silicon with clean Pd(100) between 80-1000 K reveal the formation of a quasi-stable Pd₂Si surface compound. Silane decomposes starting at 150 K. The remaining silicon or deposited atomic silicon reacts with the surface at 425 K to produce a Pd₂Si surface compound with excellent long-range order on the Pd(100) substrate. Heating to 500 K decomposes this Pd₂Si and drives silicon into the bulk (Ref. 18).*
- 16. *The adsorption, desorption, and decomposition of CH₃OH on Pd(100) using LEED, thermal desorption, UV photoemission and vibrational loss spectroscopy show the formation of a weakly bound methoxy species. A low coverage phase (2×10^{13} molecules/cm²) of methoxy species initially forms ($E_a \sim 11.5$ K cal/mole) about 50 of which can be hydrogenated and desorbed as methanol. The remaining methoxy decomposes to form CO and hydrogen. This branched reaction path for the methoxyspecies on Pd(100) provides a possible explanation for the selectivity of Pd in catalytically forming methanol from CO+H (Ref. 19).*

17. *The IBM-developed fixed angle high-resolution electron energy-loss spectrometer is made operational for surface studies (J. E. Demuth):*

- a. *Methanol decomposition studies on Pd(100) are performed as described in 3 (Ref. 19).*
- b. *Spectroscopic characterization of "Otto" peaks on Ag(111) show them to be consistent with graphitic carbon and not carbonate species (Ref. 20).*
- c. *Pyridine adsorption on Ag(111) shows a flat-lying π -bonded phase which compresses for coverages above 3×10^{14} molecules/cm² to form a 2K cal/mole weakly bound, inclined, nitrogen lone-pair bonded phase (Ref. 21).*
- d. *Benzene, cyclohexane, methanol, water, n-hexane ethylene have also been examined on Ag(111) (Ref. 22).*

18. *Angle-resolved photoemission identifies a new surface state on Ir(332), which can be unambiguously associated with step sites. This state is located near the Fermi level and can be distinguished from a terrace-related state by preferential adsorption of hydrogen on the rows of step atoms. Both states have Λ , symmetry and are located in a relative sp-hybridization gap above the L₂ point (Ref. 23).*

19. *Angle-resolved photo-stimulated desorption of oxygen ions from a W(111) surface is performed in the 2-D "photoemission" spectrometer and compared to electron-stimulated desorption. Ion angular distributions, energy distributions and photon excitation spectra for O⁺ desorption from W(111) have been measured for a wide range of oxygen coverages (Ref. 24).*

20. *Surface enhanced Raman scattering is observed from pyridine adsorbed on a Ag(111) stepped surface formed by etching weak (500Å high) 10,000Å periodicity sinusoidal profile into a Ag(111) crystal. A large mode selective enhancement (~10Å) of the Raman signal from the first monolayer is observed at surface-plasmon-polariton resonance. Coverages greater than one monolayer show a smaller enhancement (~10²) (Ref. 25).*

21. *Electron loss spectroscopy reveals new low lying electronic states for pyridine and pyrazine on an Ag(111) surface. These new states occur at 2-3 eV, are localized at the metal-molecule interface, and are attributed to metal-molecule charge transfer excitations (Refs. 26 and 27).*
22. *Electronic transitions of benzene, pyridine and pyrazine on Ag(111) have been studied. All expected intramolecular excitation of these molecules adsorbed directly on the surface are observed and lie within 0.2 eV of their free molecule values (Ref. 27).*
23. *The lifetime of excited pyrazine on Ag(111) has been determined via coverage-dependent electron energy loss measurements of the vibronic structure in the ${}^1\text{B}_{2u}$ excitation. The determined lifetimes are within a factor of 10 to those predicted by simple classical theory (Ref. 28).*
24. *Vibrational overtone spectroscopy of benzene and pyridine adsorbed on Ag(111) has been performed using electron energy loss spectroscopy. The overtone frequencies are not significantly changed for these weak adsorption systems and the overtone lifetimes are estimated (Ref. 29).*
25. *Photon-stimulated desorption from CO adsorbed on Ru(001) has been performed. This represents the first covalently bonded system to be studied by this method (Ref. 30).*
26. *Resonance electron scattering from N_2 , CO, O_2 and H_2 adsorbed on Ag has been studied. Temporary negative ion states are identified for these adsorbed species and found to occur at lower energies and have shorter lifetimes than in the gas phase (Ref. 31).*
27. *Intense low lying metal-molecule excitations are observed for CO, C_xH_y , O_2 and NC_xH_y on Ag-film evaporated at $\sim 20\text{K}$ but not on annealed or room temperature evaporated films. These results correlate well with the ability to observe SERS on evaporated films and suggest that localized (defect) sites on these films allow strong charge transfer states (Ref. 32).*

28. *Observation of rotational modes of H₂ adsorbed on Ag(111) by electron energy loss spectroscopy.* The rotational constants indicate a H-H bond length within 0.02 Å of the free molecule and show complete conversion of orthohydrogen to parahydrogen on the surface (Ref. 33).

29. *Determination of the molecular constants for molecularly adsorbed O₂ on Ag.* An analysis of the vibrational overtone spectra observed via resonance electron scattering increased anharmoniously and a reduced dissociation limit (Ref. 34).

30. *Determination of the molecular orientation of C₂H₂ on Ni(100) using impact electron scattering.* Angle-dependent electron scattering measurements and the application of impact scattering selection rules show that the mirror plane of the molecule is aligned along (110) directions and that the plane of the molecule is tilted with respect to the surface (Ref. 35).

31. *Determination of the excited state lifetimes of rare gas atoms adsorbed on Al(111), Ag(111), Cu and Au surfaces.* Electron energy loss measurements of the electronic transitions of adsorbed rare gases show broadened atomic-like transitions. Lifetimes for Ar and Xe on Al(111) are $\sim 0.2 \pm 0.1$ eV and well below those predicted theoretically (Ref. 36).

32. *LEED studies of p(2 × 2) and c(2 × 2) oxygen on Ni(100) reveal an unexpected new bonding geometry and local coordination for oxygen.* The results suggest a Jahn-Teller like distortion which results in a pseudo-bridge bonding configuration for O to Ni and a relatively short 1.85 Å O-Ni bond length (Ref. 37).

33. *Low temperature studies of the surface electronic states and transitions of the Si(111) 7 × 7 surface.* Using EELS, UPS and LEED reveal the true ridge lattice surface electronic structure. A physical different picture of the surface electronic structure emerges than deduced at room temperature (Ref. 38).

34. *Rare gas titration studies of the Si(111) 7 × 7 surface.* UPS measurements of rare gas binding energies on Si(111) provide quantitative information regarding local workfunctions of the surface as

well as qualitative information regarding geometric structure and topography of the surface (Ref. 39).

35. *Theoretical formulation of electron scattering from clean and metallic layers on semiconductor surfaces* to allow quantitative analysis and understanding of the quasielastic scattering which can occur in such systems (Ref. 40).
36. *Determination of electrical transport properties in ultrathin (~2-10 Å) metallic layers of Pd and Au on Si(111) surfaces* by electron energy loss measurements. Such "contactless" measurements enable the extension of transport measurement to ultrathin films which have not been possible with conventional measurement methods (Ref. 41).
37. *Determination of molecular and atomic oxygen species formed on Si(111) 7×7 at low temperatures (15 K)*. Two new atomic phases, a silicon monoxide diatomic molecule, and a bulk-like monoxide phase are observed to form (Ref. 42).
38. *Formation of embedded metallic microclusters on Si(111) detected upon initial Pd metallization of Si(111) at 300 K*. Frequency dependent electrical transport measurements derived from electron loss spectroscopy (Ref. 43) together with atomic hydrogen titration studies reveal this clustering (Ref. 43).
39. *First surface vibrational studies of polymer surfaces using high resolution EELS*. Several main functional groups observed with EELS and their reactions upon water removal and metal evaporation were studied (Ref. 44-45).

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